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Legacy sediments in streams - effects on nutrient partitioning during simulated re-suspension events.

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**LEGACY SEDIMENTS IN STREAMS – EFFECTS ON NUTRIENT
PARTITIONING DURING SIMULATED RE-SUSPENSION EVENTS**

A thesis submitted in partial fulfillment of the requirements for the degree of Master of
Science at Virginia Commonwealth University.

by

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Table of Contents

	Page
Acknowledgements.....	ii
Table of Contents.....	iii
List of Tables	iv
List of Figures	iv
Abstract.....	v
Introduction.....	1
Materials and Methods.....	4
Results.....	8
Discussion.....	12
Acknowledgements.....	18
Literature Cited	17
Tables and Figures	21
Vita.....	34

List of Tables

	Page
Table 1: Stream conditions at Courthouse and Kimages Creeks	21
Table 2: Regression analyses of changes in nutrient concentrations	22
Table 3: Multivariate analyses of changes in nutrient concentrations	23

List of Figures

	Page
Figure 1: Stream characteristics of Courthouse and Kimages Creeks during sampling.....	24
Figure 2: Oxygen consumption of sediments from Kimages and Courthouse Creeks	25
Figure 3: Changes in nitrogen fractions during re-suspension experiments.....	26
Figure 4: Changes in phosphorus fractions during re-suspension experiments.....	27
Figure 5: Rates of change in dissolved nutrient concentrations during re-suspension experiments	28
Figure 6: NO_x and PO_4^{3-} mineralization rates and initial suspended sediment concentration.....	29
Figure 7: Change in nitrogen fractions and particulate nitrogen concentration.....	30
Figure 8: Change in phosphorus fractions and particulate phosphorus concentration	31
Figure 9: PO_4^{3-} removed from treatment incubations	32
Figure 10: Change in phosphorus fractions and initial PO_4^{3-} concentration.....	33

Abstract

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By Molly Sobotka, B.A.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Biology at Virginia Commonwealth University.

Virginia Commonwealth University, 2011

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Anthropogenic inputs of nutrients and sediment are a widespread problem in U.S. streams causing localized impairment and contributing to eutrophication of coastal habitats. Sediments and dissolved nutrients interact through diverse processes including ion exchange, sorption and biotic assimilation by particle-bound bacteria. This study examined the effects of sediment re-suspension on nutrient partitioning in lab microcosms using fine benthic matter collected from two Virginia Coastal Plain streams. Kimages Creek was recently restored following dam removal and was characterized by large deposits of legacy sediments. Courthouse Creek was characterized by sandy substrates typical of Coastal Plain streams. Sediment characteristics differed between the

two sites and were influenced by discharge. Net nutrient release rates were similar between streams though reactivity of Courthouse Creek sediments was greater than that of Kimages Creek. Equilibrium Phosphate Concentrations calculated for each site show that fine sediments at Kimages Creek have resulted in higher phosphorus retention potential.

INTRODUCTION

Anthropogenic sources of nutrients and sediment are a widespread problem in watersheds of Chesapeake Bay and throughout the United States (Kemp et al., 2005). Nitrogen and phosphorus are of particular interest as their availability limits biotic activity in estuarine and coastal marine environments (Hasset et al., 2005). Nitrogen (N) and phosphorus (P) are transported in both dissolved and particulate phases. Dissolved forms are more directly available for biotic uptake though release of N and P contained in particulate matter may also contribute to downstream availability. For N, dissolved forms (NO_3^- , NH_4^+) typically dominate export from catchments where wastewater and agricultural sources contribute to loads (Mulholland et al., 2008). Ammonium is the more biologically desirable source of nitrogen; however nitrate pollution is more common (Webster et al., 2003, Bukaveckas et al., 2005). Phosphorus readily sorbs onto particulate matter and is therefore more commonly transported in the particulate rather than the dissolved phase. Transport is episodic, occurring during periods of elevated discharge when inputs of particulates are high and in-stream retention is low (Royer et al., 2006, Hupp et al., 2009).

Nutrient retention occurs through biotic uptake and abiotic (chemical) complexation. Biotic uptake is the assimilative removal of nutrients from the dissolved phase by autotrophic and heterotrophic members of biofilm communities (fungi, algae, and bacteria). This process temporarily sequesters nutrients in the living fraction of particulate organic matter. Assimilation is offset by re-mineralization during decomposition; the balance between these two processes determines net retention (Fisher et al., 1998). Chemical complexation includes cation exchange,

in which ammonium can exchange with positive ions associated with negatively charged sites on particles. Sorption-desorption reactions are abiotic processes by which anions (predominantly phosphates) are bonded or released from adsorption sites on particles. Cation exchange and sorption-desorption reactions are reversible; their rate and direction are governed by ambient concentrations of the dissolved reactants and the number and availability of exchange and sorption sites (James and Barko, 2004, Wang et al., 2007). The Equilibrium Phosphate Concentration (EPC_0) is the theoretical point at which no net sorption or desorption of PO_4^{3-} onto sediments takes place. At concentrations higher than the EPC_0 , PO_4^{3-} is generally sorbed to sediments and at lower concentrations PO_4^{3-} de-sorbs from sediments (Webster et al., 2001). The EPC_0 is a useful tool for understanding the potential for P sequestration and release under varying conditions of sediment and nutrient concentrations.

Biotic uptake and chemical complexation delay the transport of nutrients downstream through biomass accumulation and short-term storage of particulate matter. In the case of N, denitrification to N_2 gas can eventually lead to permanent removal (i.e., loss to the atmosphere) via (Royer, 2004). Nutrient loading to streams is often accompanied by enhanced sediment loading (Paul and Meyer, 2001, Palmer-Felgate et al., 2009) though few studies have considered the combined effects of these two stressors on nutrient retention (Mulholland and Webster, 2010). In streams, studies of sediment-water interactions are typically conducted during low discharge conditions and therefore do not take into account effects during periods of high suspended sediment loads. Prior studies of sediment re-suspension have focused on estuarine and lake environments. Re-suspending sediments on the floor of the Gulf of Finland (Baltic Sea) resulted in greater dissolved oxygen consumption and increased ammonium concentrations but did not affect nitrate or phosphate concentrations (Almroth et al., 2009). In contrast, de Vicente

et al. (2010) showed that sediment re-suspension by wave action in two shallow lakes caused sediments to either release or adsorb PO_4^{3-} . Variation in phosphate release from sediments was attributed to substrate composition and water column PO_4^{3-} concentration. Griffin and Corbut (2003) found that phosphate and ammonium fluxes in the Neuse/Pamlico River Estuary were elevated to six times average values during re-suspension events due to release from pore water.

Streams of the Virginia Coastal Plain are characterized by sandy substrates that have high hydraulic conductivity and are prone to disturbance at relatively low water velocities (Hupp, 2000). Low substrate stability can limit opportunities for the establishment of biofilms, thus reducing biotic uptake. Many streams in the region are characterized by the presence of legacy sediments, which are remnants of historical erosive events. These deposits can persist even after mitigation of land use activities and in-stream restoration (e.g., dam removal; Doyle et al., 2005, Walter and Merritts, 2008, Schenk and Hupp, 2009). There are a number of mechanisms by which the presence of legacy sediments can alter nutrient dynamics in streams. The compactness of fine substrates results in low hydraulic conductivity, limiting the vertical movement of water through the streambed (Wood, 1997, Nogaro et al., 2010). This in turn can limit the interaction between dissolved nutrients and hyporheic microbial communities, an important site for biogeochemical processes in streams (Fuss and Smock 1996; Fisher, 1998). When fine sediments are suspended into the water column via overland flow, bank erosion, or re-suspension, their slow settling rate can inhibit light penetration to the benthos and thus photoautotrophic components of biofilms (Wood, 1997). Other characteristics of legacy sediments may enhance nutrient retention. For example, the greater surface area of fine sediments may allow for greater cation exchange and adsorption during re-suspension events. A number of studies have documented the importance of clay particles as sorption sites for phosphorus, though less is

known regarding their role in cation exchange (de Vicente et al., 2010). Lastly, the clay component of legacy sediments increases cohesion and in areas where compaction of sediments has occurred may provide a more stable substrate for biofilm colonization. This can also impede the flushing of interstitial spaces, resulting in large differences between pore water and water column nutrient concentrations.

The goal of this study was to assess the effects of sediment type on stream nutrient chemistry during simulated re-suspension events. It was hypothesized that re-suspending sediments will alter the concentration of nutrients in the dissolved and particulate phases but that these effects will differ depending on sediment composition. Re-suspension of fine (legacy) sediments was predicted to result in lower nutrient concentrations in the dissolved phase in comparison to the re-suspension of coarse (sandy) sediments due to higher rates of cation exchange and P sorption.

METHODS

This study used a paired-stream comparative approach to assess sediment-nutrient interactions at two sites that differ in substrate composition. One site (Kimages Creek) is dominated by fine-grained, legacy sediments that accumulated during a period when the stream was impounded (1927-2007). The other site (Courthouse Creek) is a sandy-bottomed stream typical of the Virginia Coastal Plain (Hupp, 2000). Sediment re-suspension experiments were performed in the laboratory using water and sediments collected from the two sites. Effects of sediment re-suspension on nutrient partitioning between the dissolved and particulate phases were determined by measuring changes in dissolved and total nitrogen and phosphorus

concentrations at the start and end of the 6-day incubation period. Experiments were performed at 1- and 2- month intervals between June 2010 and March 2011. Results from individual experiments were pooled so that changes in nutrient concentrations across experiments could be analyzed in relation to seasonal and inter-site variation in sediment mass and composition (C, N, and P content).

Study Sites

Kimages and Courthouse Creeks are tributaries of the James River located in Charles City County, Virginia. Water and sediment samples from Kimages Creek were collected at Virginia Commonwealth University's Rice Center. Courthouse Creek is located 13 km east and was sampled adjacent to the Charles City County Public School. The lower segment of Kimages Creek is the site of a former impoundment (Lake Charles). In October of 2007, a breach in the dam resulted in a draw-down of the lake and allowed the creek to reestablish flow in its historic channel. The restored segment of Kimages Creek is ca. 2 km in length and is characterized by fine sediment (clay, silt), which is a legacy of the former impoundment (Figure 1). Data on water quality and nutrient concentrations collected in this and previous studies were used to characterize the two study sites (Table 1). The streams are dilute (low conductivity), moderately acidic ($\text{pH} < 6.5$), and well oxygenated. Courthouse Creek had higher concentrations of NO_x and PO_4^{3-} than Kimages and lower levels of NH_4^+ . Dissolved organic carbon (DOC) concentrations were similar between sites.

Field and Laboratory Methods

Sampling methods to obtain fine benthic material (FBM) were adapted from Mulholland et al. (2001). A sampling enclosure (33-cm diameter) was inserted into the stream bottom and sediments were suspended by hand into the overlying water. Samples of water and sediment

were returned to the laboratory for incubation experiments. Stream temperature, dissolved oxygen, specific conductivity, and pH were measured concurrent with sample collection. Turbidity was measured within the sampling enclosures in order to compare the simulated sediment re-suspensions with in-stream conditions. In Kimages Creek, turbidity during simulated re-suspensions ranged from 704 to 1505 NTU (mean = 1191 NTU). This range of values corresponds to the top 10%-tile of in-stream values recorded near the sampling site by a permanently placed YSI sonde. Turbidity in Courthouse Creek enclosures averaged 420 NTUs (range = 57 to 837 NTU).

In the laboratory, 6 100-mL aliquots of water and sediment from each site were placed in 250-mL Erlenmeyer flasks. 3 replicates were immediately processed to characterize initial conditions while 3 replicates were placed on a platform shaker at 170 rpm for 6 days. Incubations were performed in the dark at ambient (stream) temperatures in a Conviron Growth Chamber. Initial and final samples were analyzed for concentrations of suspended sediments, the C and N content of suspended sediments and total and dissolved N and P fractions (TN, TP, NO_x , NH_4^+ , and PO_4^{3-}). Samples for suspended sediment analyses were filtered through pre-weighed and pre-combusted GF-A glass fiber filters. These filters were dried for 2 days at 70 °C and re-weighed to calculate the mass of suspended sediment. Filters for suspended sediment determinations were also used for organic carbon and nitrogen analyses on a Perkin-Elmer CHN analyzer. Total suspended sediment concentrations and their C and N content were used along with the area of the sampling enclosures to calculate areal sediment mass, C and N (as g/m^2).

Sediment oxygen demand was measured as an indicator for the presence of labile organic matter in suspended sediments. Water and sediments obtained from the sampling enclosure were placed in 60-mL BOD bottles and incubated for 6 days in the dark at ambient (stream)

temperature. Dissolved oxygen concentrations were determined at days 0 and 6 by micro-Winkler colorimetric titration (Carignan, 1998). Results were expressed as the rate of oxygen change per unit volume and per unit of sediment mass.

All nutrient fractions were determined from colorimetric reactions using a Skalar auto-analyzer. Particulate nitrogen (PN) and phosphorus (PP) concentrations were calculated as the difference between total and total dissolved concentrations. Dissolved organic nutrient concentrations were calculated as the difference between total dissolved nutrients and the sum of all dissolved inorganic fractions. To check the quality of our data we compared the mass of N and P recovered at the end of the incubation with starting concentrations. For N, the total mass in various fractions corresponded to 102 % (Courthouse) and 105 % (Kimages) of starting concentrations. We can account for the fate of all initial nitrogen in experiments suggesting that loss of N via denitrification to N_2 was not a significant pathway of loss. For P, 82 % (Courthouse) and 105 % (Kimages) of starting concentrations were recovered at the conclusion of the experiment. Thus, a portion of phosphorus in some Courthouse incubations was not accounted for.

Phosphorus Manipulation Experiments

In addition to incubating sediments at ambient nutrient concentrations, P amendment experiments were conducted to determine the EPC_0 of sediments from both sites. Preliminary trials were conducted in January, with additions of 100 $\mu\text{g/L}$ of phosphate from KPO_4 . In March, phosphate was added to increase initial concentrations by 100 (Low treatment), 300 (Medium treatment), and 600 $\mu\text{g/L}$ (High treatment). To reduce ambient PO_4^{3-} , 50-mL samples of stream water and sediment were diluted with 50-mL of de-ionized water. Samples were incubated for 6 days in a Conviron Growth Chamber at ambient (*in situ*) temperature. The EPC_0 's for Courthouse

and Kimages were calculated from regressions of change in particulate P vs. initial dissolved P using data from the P amendment experiment conducted in March (method adapted from Smith et al., 2005).

Data Analyses

Pair-wise differences between initial and final nutrient concentrations were used to determine rates of change in concentrations during the 6-day experiments. ANOVA was used to partition intra- and inter- experimental variation in rates of change for the various nutrient fractions (dissolved inorganic, dissolved organic, particulate and total). Location (i.e., Site) was used as a categorical predictor to assess differences in treatment effects among experiments conducted at Kimages and Courthouse Creeks. Site-specific attributes (e.g., sediment mass and composition) were tested in multivariate regressions to identify potentially important factors affecting sediment-nutrient interactions.

RESULTS

Site Comparison

The sites selected for this study are not gauged so discharge values from a nearby site (Totopotomoy Creek, VA) were used to broadly characterize seasonal variation. Among months in which sediment experiments were performed, highest discharge occurred in October and January (Figure 1). As the reference site has a larger watershed, the discharge values are not representative of Courthouse and Kimages. Prior research showed that discharge in Courthouse Creek ranged from 24 to 78 L/s and averaged 48 L/s over a period of 7 months (Frank, 2009). In

Kimages Creek discharge averaged 38 L/s over an annual cycle (range = 8.4 to 75 L/s; Wood, 2010).

The mass and composition of sediments differed between sites and among months. Sediment mass was on average two-fold higher at Kimages (mean = $543 \pm 94 \text{ g/m}^2$) relative to Courthouse (mean = $244 \pm 90 \text{ g/m}^2$). Sediment mass was similar at both sites in June, however in all other months Kimages had greater sediment concentrations. Greater seasonal variation in sediment mass was observed at Courthouse (range = 38 to 531 g/m^2) than at Kimages (range = 216 to 822 g/m^2). Sediment was lowest at both sites in October and January when discharge was highest. The average C% and N% of Courthouse sediments (mean = 4.5 ± 1.2 and $0.35 \pm 0.11 \%$, respectively) was twice as high as in Kimages sediments (mean = 1.9 ± 0.4 and $0.17 \pm 0.04\%$, respectively). Despite the lower proportion, the areal mass of C and N was higher at Kimages (mean = $12.3 \pm 0.8 \text{ g C/m}^2$ and $1.2 \pm 0.1 \text{ g N/m}^2$) relative to Courthouse (mean = $8.3 \pm 2.8 \text{ g C/m}^2$ and $0.6 \pm 0.2 \text{ g N/m}^2$) due to the greater overall sediment mass. With the exception of one sampling date (November), Kimages sediments had a consistently greater oxygen demand, indicating the presence of more labile organic matter (Kimages = $0.82 \pm 0.1 \text{ mg L}^{-1} \text{ d}^{-1}$, Courthouse = $0.54 \pm 0.1 \text{ mg L}^{-1} \text{ d}^{-1}$; Figure 2). At Courthouse, variation in sediment oxygen demand was mostly explained by temperature ($R^2 = 0.75$, $p = 0.021$), though this relationship was not significant at Kimages.

The relative contributions of dissolved and particulate fractions to total nutrients differed among sites and months. Average TN was similar between sites (Kimages = $2.19 \pm 0.24 \text{ mg/L}$, Courthouse = $2.16 \pm 0.34 \text{ mg/L}$); however, at Kimages, N was dominated by the particulate fraction (56-79% of total, average = 71%) whereas at Courthouse, particulate N was more variable (13-87%, average = 55%; Figure 3). NO_x concentrations at Courthouse (average = 0.45

± 0.18 mg/L) corresponded to 23% of TN and were generally higher than those of Kimages (average = 0.30 ± 0.07 mg/L; 12% of TN). Total P was also similar between sites (Kimages = 0.51 ± 0.11 mg/L, Courthouse = 0.42 ± 0.08 mg/L). Particulate P was more variable at Courthouse and accounted for the majority of P at both sites (Courthouse: 22-91%, average = 77%; Kimages: 79-97%, average = 89%; Figure 4). Dissolved organic and inorganic P was generally lower in Kimages than in Courthouse and no seasonal patterns were apparent.

Re-suspension Experiments

Rates of change of nutrient concentrations were determined from the difference between final and initial concentrations after 6-day incubations. Positive rates represent a net gain within a specific fraction (e.g., NO_x) whereas negative rates indicate a net loss (decrease in concentration). Changes in NO_x concentrations were positive in 4 of 6 experiments with similar rates observed at the two sites (Kimages = -13 to $58 \mu\text{g L}^{-1} \text{d}^{-1}$, Courthouse = -2 to $49 \mu\text{g L}^{-1} \text{d}^{-1}$; Figure 5). Highest rates of nitrate production at both sites occurred in June and August. Changes in NH_4^+ concentrations were positive in most experiments with highest rates observed in August and October at Kimages Creek (Kimages = 3.6 to $94.7 \mu\text{g L}^{-1} \text{d}^{-1}$, Courthouse = -5.9 to $12.1 \mu\text{g L}^{-1} \text{d}^{-1}$). Rates of change of PO_4^{3-} concentrations were generally positive in Courthouse experiments and more variable in Kimages experiments (Figure 5). The range of rates of PO_4^{3-} change were similar at the two sites (Kimages = -2.0 to $1.8 \mu\text{g L}^{-1} \text{d}^{-1}$, Courthouse = -2.5 to $3.8 \mu\text{g L}^{-1} \text{d}^{-1}$). As was the case for NO_x , Courthouse exhibited higher rates of PO_4^{3-} production during the June and August experiments, whereas Kimages did not exhibit a consistent seasonal trend. Overall, the experiments revealed seasonal trends in the effects of sediment re-suspension on dissolved nutrient concentrations but little difference between the two sites.

Changes in the dissolved inorganic fractions were analyzed in relation to initial incubation conditions (suspended sediment, particulate C, N, and P, dissolved nutrient concentrations, and temperature, Table 2) as well as changes in other fractions (particulate N and P and DON and DOP). For Courthouse, a number of factors were significant predictors of variation in NO_x release. These included the initial concentration of suspended sediments ($R^2 = 0.91$; Figure 6) and the initial concentration of particulate N ($R^2 = 0.73$; Figure 7). The correlations were positive indicating that greater amounts of particulate material led to higher final concentrations of NO_x . Changes in DON were negatively associated with initial PN concentrations though the relationship was not statistically significant. At Kimages, temperature was a significant predictor of variation in NO_x release ($R^2 = 0.69$); however a multivariate model using both temperature and PN explained more variation ($R^2 = 0.93$; Table 3). A significant negative relationship between change in NH_3 concentrations and change in NO_x was observed at Courthouse Creek ($R^2 = 0.67$) and a multivariate model with initial PN and change in NH_4^+ accounted for most NO_x variation ($R^2 = 0.90$).

Initial suspended sediment concentrations were a significant predictor of rates of change in PO_4^{3-} concentrations at Courthouse ($R^2 = 0.76$; Figure 6). Rates of change of PO_4^{3-} concentrations in Courthouse incubations were also correlated with temperature ($R^2 = 0.67$; Table 2). The initial amount of particulate P present at the start of the incubation was a predictor of the rate of change in PP in Courthouse incubations ($R^2 = 0.74$; Figure 8) and of DOP ($R^2 = 0.64$). Decreases in PP were correlated with an increase in DOP ($R^2 = 0.73$, Table 2). PP concentration was not a significant predictor of change in PO_4^{3-} concentration at either site. However, initial PP was strongly correlated with the rate of change in dissolved organic phosphorus concentrations at Kimages ($R^2 = 0.67$). Overall, meta-analyses of rates of change

among nutrient fractions revealed that sediment properties were important predictors of variation in Courthouse nutrient transformation rates. Changes in Kimages nutrient concentrations varied independently from sediment characteristics.

Phosphate Manipulation Experiments

Phosphate was lost in all treatments except dilutions with losses increasing in response to the amount of PO_4^{3-} added (Figure 9). The two sites differed in response to increasing levels of PO_4^{3-} addition as a saturation effect was observed at Courthouse (maximum removal = 50%) whereas Kimages sediments removed increasingly large percentages of phosphate (84% at highest addition). Though proportions differed, maximum uptake rates were similar (Courthouse = $0.037 \text{ mg L}^{-1} \text{ d}^{-1}$, Kimages = 0.039 mg/L/d) because initial concentrations of PO_4^{3-} were lower at Kimages. Initial phosphate concentration predicted increases in dissolved organic phosphorous and particulate P concentrations in Courthouse incubations (Figure 10). The proportions of phosphate lost to DOP and particulate P fractions differed between sites and among treatments. At Courthouse, increases in DOP accounted for 25-35% of PO_4^{3-} removal in Medium and High phosphate treatments. At Kimages, High treatments resulted in increases in particulate P only while rates of DOP change were close to zero. Conversely, in the Medium PO_4^{3-} treatment, DOP concentrations increased and there was no change in particulate P. The EPC_0 of sediments at Courthouse Creek was 0.090 mg/L and the value found at Kimages was 0.010 mg/L .

DISCUSSION

Contrary to our hypothesis, rates of change per unit of sediment were typically higher in incubations of coarse sediments from Courthouse Creek. At this site, rates of change in dissolved

N and P fractions were significantly correlated with sediment properties including sediment mass, PN and PP. At Courthouse Creek, sediment mass and areal mass of C and N were seasonally variable and particulate nutrients accounted for less of the total nutrient fraction. Discharge was an important determinant of sediment characteristics at this site. The months of October and January had the highest discharge and correspondingly low sediment and nutrient (C, N, and P) concentrations. Sediment mass at Courthouse did not recover to pre-October values during the period of this study, whereas sediment mass at Kimages Creek returned to previous levels within one month. Further hydrological data are needed to determine the differing mechanisms of stream response to storm events. However, this study shows that storm events can have important and lasting implications for nutrient retention via effects on sediment characteristics.

Per unit sediment removal rates of O_2 by Courthouse sediments were higher than those of Kimages sediments. The greater relative amount of organic material in Courthouse sediments could allow for higher rates of respiration. The disparity in concentrations of organic material could be caused by more efficient trapping of organic material in the larger interstitial spaces found between coarse particles as suggested by Harvey et al. (2011).

Both mineralization of organic N from sediments into NO_x and nitrification of NH_3 to NO_x are important pathways of NO_x production that can occur under dark conditions (Penderson et al., 1999, Kreiling et al., 2011). Correlations between initial concentrations of particulate nitrogen and change in NO_x concentrations in incubations of sediments from both sites were observed, suggesting that mineralization was an important source of inorganic N. Higher rates of NO_x production correspond to low NH_3 production in Courthouse incubations suggesting that nitrification of NH_3 to NO_x was an important pathway. Changes in NH_3 and NO_x were not

related in Kimages incubations, indicating that mineralization of sediment and abiotic release of NH_3 were the main sources of inorganic N. Initial NH_3 conditions in Kimages, August incubations were higher than average (0.12 mg/L) and it is likely that pore water and sediment concentrations of NH_3 were even higher (Wang et al., 2008). Particulate N was also above average during the August experiment. Sediment release of NH_3 can be stimulated by agitation (Yin and Harrison, 2000) suggesting that the high initial concentration in August was a result of release following sample collection. Release of NH_3 during incubation was likely due to sediment exposure to water column NH_3 concentrations lower than concentrations found in pore water.

Areal rates of NO_x production in this study were calculated as the product of the rate of NO_x production per unit sediment and the areal mass of sediment. NO_x production was estimated to range from -0.6 to 15.7 $\text{mg N m}^{-2} \text{d}^{-1}$ in Courthouse and from -4.5 to 21.3 $\text{mg N m}^{-2} \text{d}^{-1}$ in Kimages. These rates reflect net NO_x production (combined mineralization of organic N and nitrification of NH_3), further studies including isotope-labeled nitrogen additions of PON or NH_3 could determine separate rates of NO_x and NH_3 release from sediments and nitrification. Using increases of ^{15}N labeled NO_3^- during a ^{15}N -ammonium release study Webster et al. (2003) found stream nitrification rates for benthic sediments ranging from 2.0 to 28 $\text{mg N m}^{-2} \text{d}^{-1}$, similar to net NO_x production observed in this study. Net nitrification rates of sediment N and NH_3 as high as 61 $\text{mg N m}^{-2} \text{d}^{-1}$ have been observed in undisturbed lake sediments (Kreiling et al., 2011). A laboratory study on nitrogen cycling in coarse and fine sediments also found similar rates of NO_x production (coarse = 36 $\text{mg N m}^{-2} \text{d}^{-1}$, fine = 23 $\text{mg N m}^{-2} \text{d}^{-1}$; Harvey et al., 2011) suggesting that re-suspension of sediments does not affect nitrification.

Changes in PO_4^{3-} concentrations were not related to any variable measured in this study; however, DOP concentrations increased with initial particulate P concentrations at both sites. At ambient PO_4^{3-} concentrations, re-suspension results in the release of organic phosphorus from the particulate fraction rather than the release of PO_4^{3-} . Two possibilities could account for the increase in DOP: (i) biotic uptake of dissolved P or (ii) abiotic complexation between PO_4^{3-} and dissolved organic compounds. Future studies should examine the difference in PO_4^{3-} uptake rates in stream water and combined stream and sediment mixtures. If DOC is a PO_4^{3-} sink, some uptake may occur without the presence of sediment. The relationship between temperature and PO_4^{3-} release suggests that microbial breakdown of sediment organic material is important on Courthouse sediments. Summer experiments had the greatest concentrations of particulate P and of organic material providing the greatest opportunity for PO_4^{3-} desorption and large amounts of material to microbes, resulting in the large Courthouse PO_4^{3-} releases seen in August and June.

The EPC_0 concentration calculated for Kimages was almost an order of magnitude lower than that found for Courthouse. This finding supports my hypothesis that the greater number of sorption/desorption sites found on the fine legacy sediments at Kimages would result in greater PO_4^{3-} retention. Clay and silt deposits, known to have a higher affinity for abiotic P uptake (de Vicente et al., 2010) are present in higher concentrations at Kimages than Courthouse (Brandt, 2009). Initial PO_4^{3-} concentrations in Courthouse incubations and average ambient conditions in Courthouse were consistently lower than the calculated EPC_0 suggesting that Courthouse sediments were generally a source of PO_4^{3-} . Conversely, initial Kimages PO_4^{3-} concentrations were at or higher than the EPC_0 of 0.010 mg/L. Thus, Kimages sediments should generally be a sink for PO_4^{3-} . Uptake did occur when initial PO_4^{3-} concentrations were close to the EPC_0 and when particulate P concentrations were highest. Concentrations of PP can be higher than those

found in the upper water column (Webster et al., 2001). Saturation of P sorption sites can result in higher EPC_0 's (Hoffman et al., 2009) and thus sediments that are more likely to release PO_4^{3-} .

EPC_0 for Kimages was similar to values found for wetlands (0.01 mg/L, Zhang, 2011) and streams minimally impacted by agriculture (0.003 to 0.013 mg/L, Palmer-Felgate et al., 2009; 0.003 to 0.007 mg/L, Sutter et al., 2008). Palmer-Felgate et al. (2009) found that highly impacted agricultural streams had EPC_0 's of 0.016 to 0.079 mg/l, similar to the value found for Courthouse Creek. EPC_0 values found for large river systems were similar to the value found for Courthouse (Spree River EPC_0 = 0.054 to 0.127 mg/L, Schulz and Herzog, 2004) or much higher (Minnesota River EPC_0 = 0.155 mg/L, James and Barko, 2004). Palmer-Felgate et al. (2009) found that impacted streams also had higher P inputs from catchments, more fine sediments, and that high PO_4^{3-} water column concentrations could result in higher EPC concentrations. The higher ambient concentrations of PO_4^{3-} in Courthouse Creek likely also contribute to the higher EPC_0 . It is important to note that the EPC_0 's found in this study may not be accurate in non-re-suspension conditions. Anoxia developing in undisturbed sediments can result in higher EPC_0 values (House and Denison, 2000). Thus, *in situ* the compactness of Kimages sediments may cause less efficient P retention.

The results of this study show that sediment mass, composition, and particulate nutrient concentrations were different between sites. Reactivity of Courthouse sediments was greater than that of Kimages sediments, likely because of relatively greater amounts of organic material present in the stream bed. Particulate N and P concentrations were important factors in nutrient change rates in Courthouse incubations. It is possible that the relationships between nutrient changes and particulate concentrations were evident at Courthouse because of the greater variability of particulate nutrient fractions observed. Minimum particulate N and P

concentrations at Courthouse were lower than those found at Kimages and were as low as 10% of total P and 22% of total N. Particulate nutrient concentrations in Kimages incubations were likely never small enough to limit nutrient production. I postulate that either (i) sediment removed during high flow events can be immediately replaced by erosion and incisement at Kimages, as seen in other previously dammed streams (Schenk and Hupp, 2009) whereas only larger sediments remain at Courthouse or (ii) that the geomorphology of Kimages prevents intense scour events from occurring. The now exposed lakebed may provide a floodplain sufficient to reduce flood intensity or beaver dams downstream of the sampling site may reduce water velocity such that sediment transport is significantly impeded.

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Table 1. Stream conditions at Courthouse and Kimages Creeks. Data shown are average values for January to August 2008 ('a'; n=20), February 2010 to January 2011 ('b'; n=20) and June 2010 to March 2011 ('c'; n=6). 'a' and 'b' from Frank (2009); 'c' from this study.

	Courthouse Mean (SE)	Kimages Mean (SE)
NOx (mg/L)	0.420 (0.052) ^a	0.271 (0.048) ^b
NH3 (mg/L)	0.034 (0.005) ^a	0.053 (0.009) ^b
PO4 (mg/L)	0.036 (0.006) ^a	0.013 (0.002) ^b
DOC (mg/L)	4.46 (1.13) ^a	3.12 (0.62)
DO (mg.L)	6.71(0.31) ^c	6.39(0.22) ^c
SpCond (μS/cm)	88(3) ^c	104(4) ^c
pH (units)	6.33 (0.09) ^c	5.86 (0.06) ^c

Table 2. Regression analyses of changes in nutrient concentrations during 6-day re-suspension experiments using sediment from Kimages and Courthouse Creeks and initial incubation conditions.

	Suspended sedimen		Initial PN		Initial PP		Initial Nox		Initial NH ₄		Initial PO ₄		Temp	
	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value	R ²	p-value
Kimages														
ΔNOx	0.26	0.635	0.05	0.677	0.10	0.548	0.78	0.020	0.01	0.845	0.80	0.0154	0.69	0.040
ΔNH ₄	0.23	0.334	0.42	0.166	0.00	0.949	0.03	0.746	0.18	0.401	0.11	0.515	0.94	0.386
ΔDON	0.03	0.745	0.23	0.338	0.17	0.420	0.07	0.615	0.380	0.193	0.45	0.143	0.63	0.0598
ΔPN	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
ΔPO ₄	0.19	0.391	0.00	0.991	0.00	0.975	0.27	0.287	0.06	0.641	0.46	0.139	0.11	0.524
ΔDOP	0.01	0.854	0.38	0.195	0.67	0.046	0.70	0.039	0.18	0.401	0.35	0.219	0.12	0.495
ΔPP	0.10	0.552	0.53	0.100	0.58	0.077	0.2566	0.305	0.64	0.0543	0.00	0.918	0.02	0.892
ΔDO	0.24	0.329	0.04	0.716	0.28	0.276	0.066	0.622	0.06	0.648	0.07	0.601	0.26	0.303
Courthouse														
ΔNOx	0.99	<0.001	0.84	0.099	0.64	0.569	0.21	0.357	0.63	0.427	0.06	0.628	0.45	0.154
ΔNH ₄	0.62	0.062	0.49	0.122	0.22	0.351	0.66	0.050	0.16	0.435	0.42	0.554	0.50	0.114
ΔDON	0.40	0.177	0.46	0.140	0.25	0.309	0.03	0.751	0.00	0.979	0.41	0.168	0.30	0.263
ΔPN	0.00	0.946	0.09	0.559	0.01	0.883	0.16	0.434	0.24	0.322	0.03	0.724	0.13	0.489
ΔPO ₄	0.72	0.032	0.63	0.058	0.34	0.221	0.12	0.495	0.01	0.832	0.07	0.621	0.07	0.045
ΔDOP	0.49	0.366	0.34	0.227	0.64	0.057	0.06	0.641	0.15	0.456	0.08	0.596	0.04	0.690
ΔPP	0.82	0.013	0.09	0.559	0.74	0.029	0.1	0.535	0.02	0.799	0.16	0.424	0.41	0.169
ΔDO	0.19	0.390	0.01	0.859	0.04	0.706	0.42	0.165	0.23	0.341	0.02	0.804	0.75	0.027

Table 3. Multivariate regression analyses of changes in nutrient concentrations and results from P addition experiments.

Experiment	Variable	Model	R ²	p-value
Kimages				
all months	ΔNO _x	= 0.003*Temp - 0.0229*initial PN + 0.004	0.93	0.017
PO ₄ addition	ΔPO ₄	= -0.145*initial PO ₄ + 1.528	0.99	<0.0001
PO ₄ addition	ΔPP	= 0.105*initial PO ₄ - 1.054	0.49	0.011
Courthouse				
all months	ΔNO _x	= -2.622*ΔNH ₃ + 27.456	0.67	0.047
all months	ΔNO _x	= -1.108*ΔNH ₃ + 16.228*initial PN + 1.826	0.90	0.03
all months	ΔDOP	= -0.408*ΔPP - 0.004	0.73	0.03
PO ₄ addition	ΔPO ₄	= -0.091*initial PO ₄ + 0.600	0.99	<0.0001
PO ₄ addition	ΔDOP	= 0.021*initial PO ₄ + 1.194	0.83	<0.001
PO ₄ addition	ΔPP	= 0.111*initial PO ₄ - 9.989	0.87	<0.001

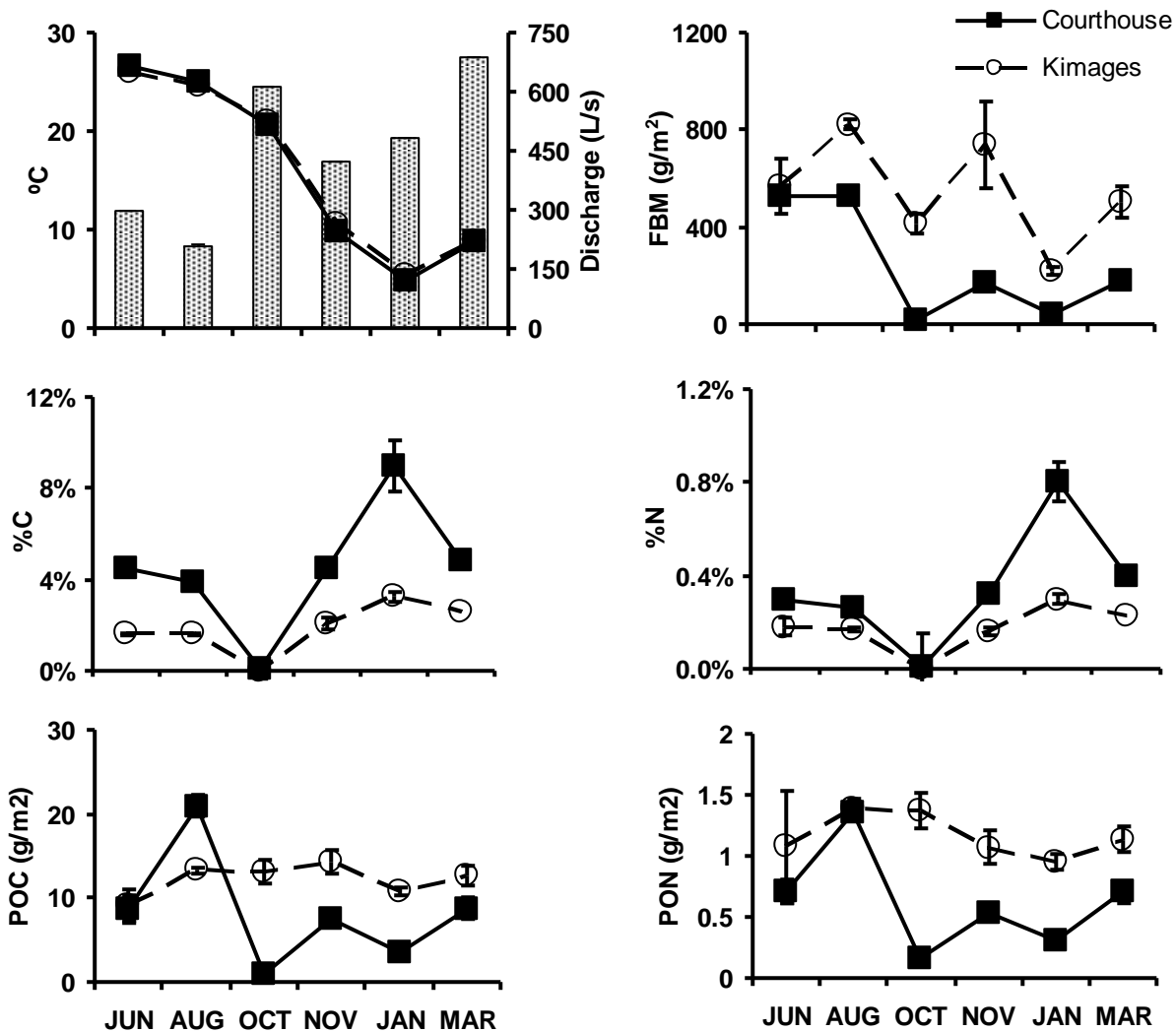


Figure 1. Stream and sediment characteristics of Courthouse and Kimages Creeks during June 2010 through March 2011. Error bars represent one standard error. Discharge data are for nearby USGS gauge at Totopotomoy Creek, VA.

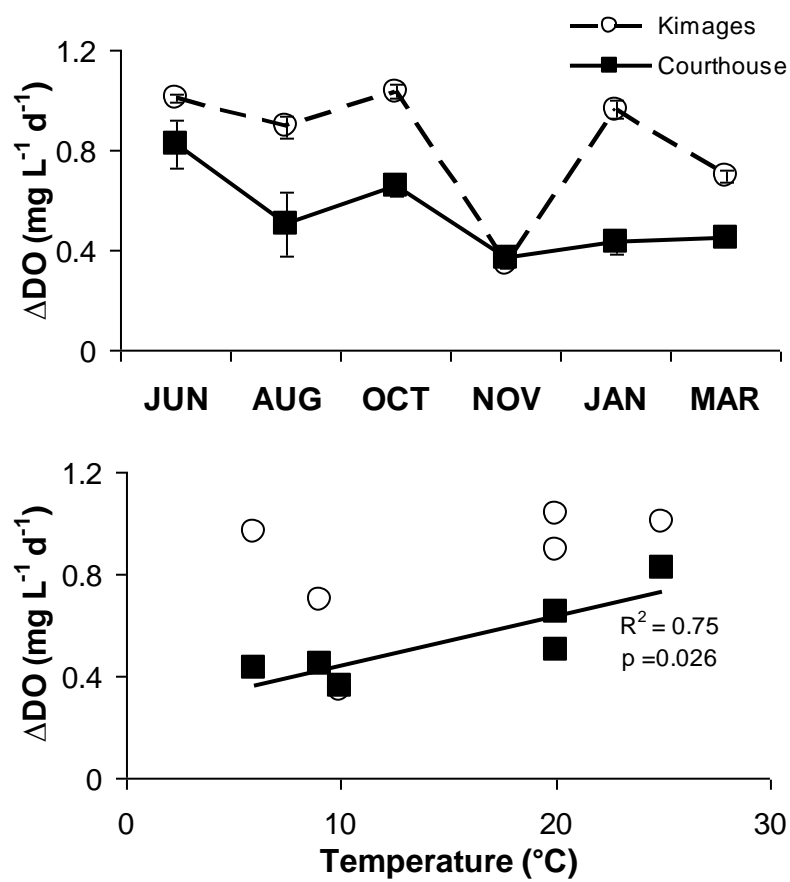


Figure 2. Seasonal variation in oxygen consumption of sediments from Kimages and Courthouse Creeks and the relationship between oxygen consumption and temperature.

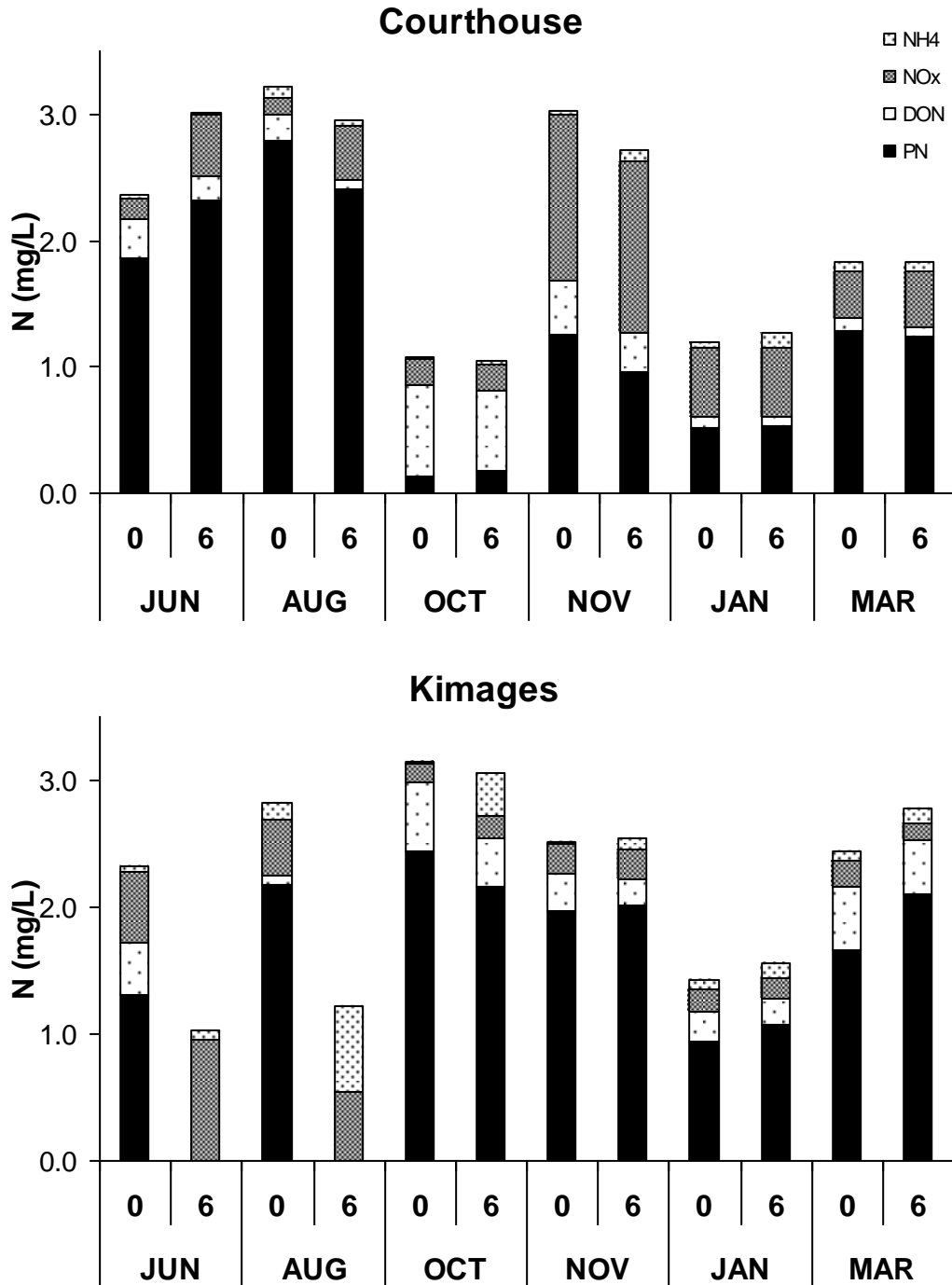


Figure 3. Changes in nitrogen fractions during 6-day sediment re-suspension experiments performed in the laboratory.

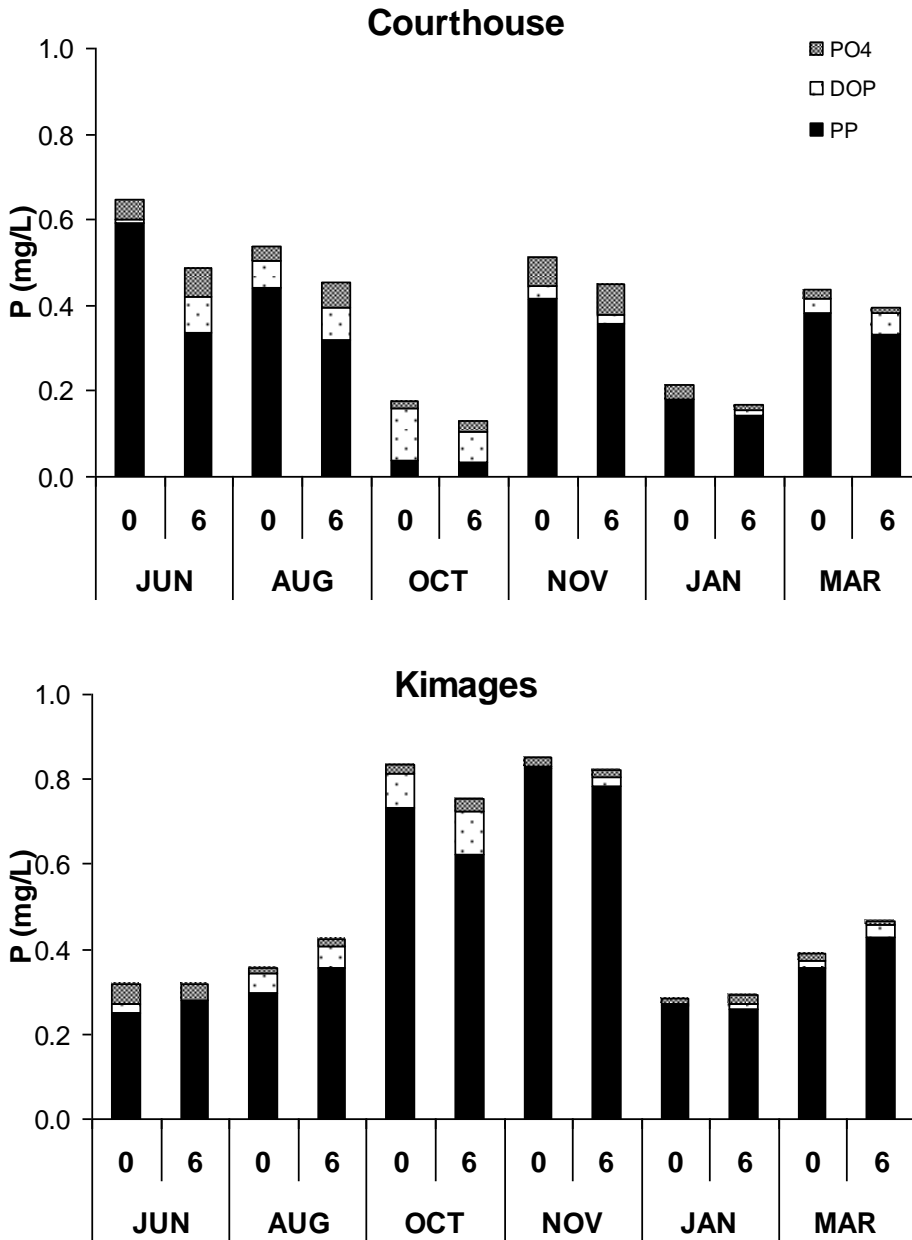


Figure 4. Changes in phosphorus fractions during 6-day sediment re-suspension experiments performed in the laboratory.

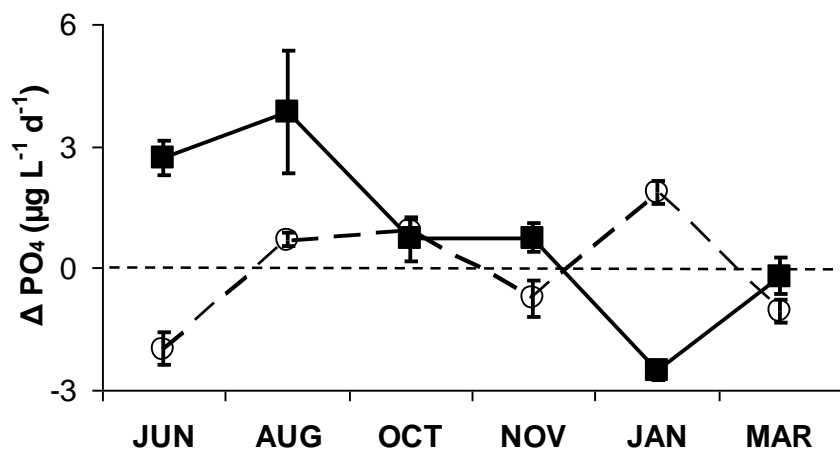
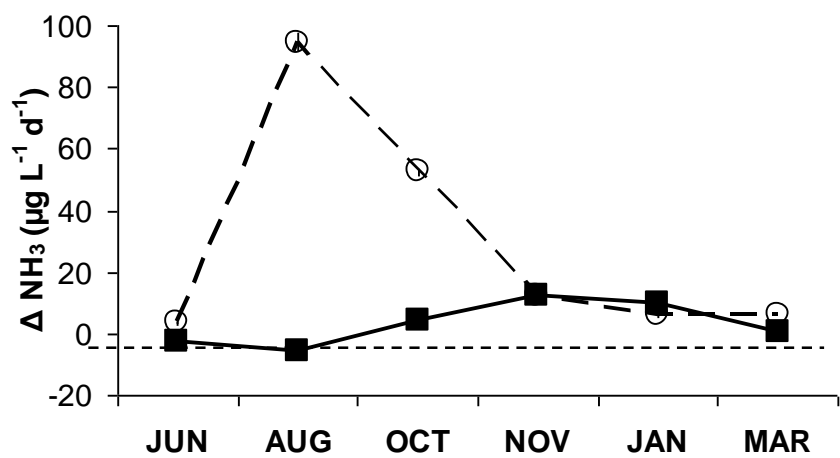
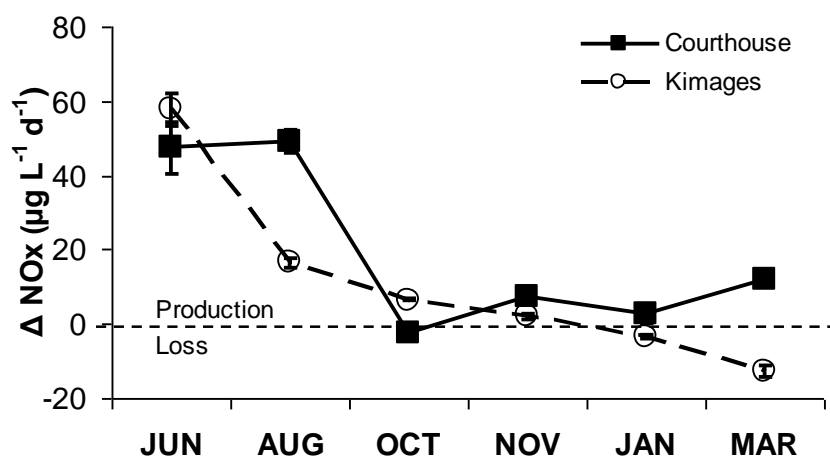


Figure 5. Rates of change in dissolved nutrient concentrations during 6-day sediment re-suspension experiments. Note differing y-axis scales. Error bars represent one standard error.

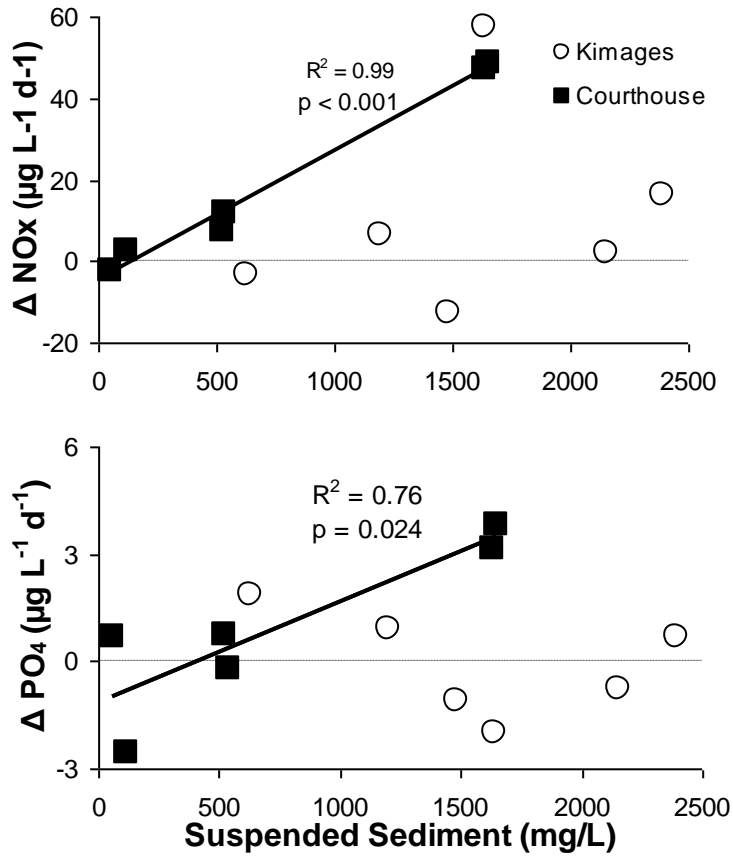


Figure 6. Relationship between NO_x and PO_4^{3-} mineralization rates and initial suspended sediment (mg/L).

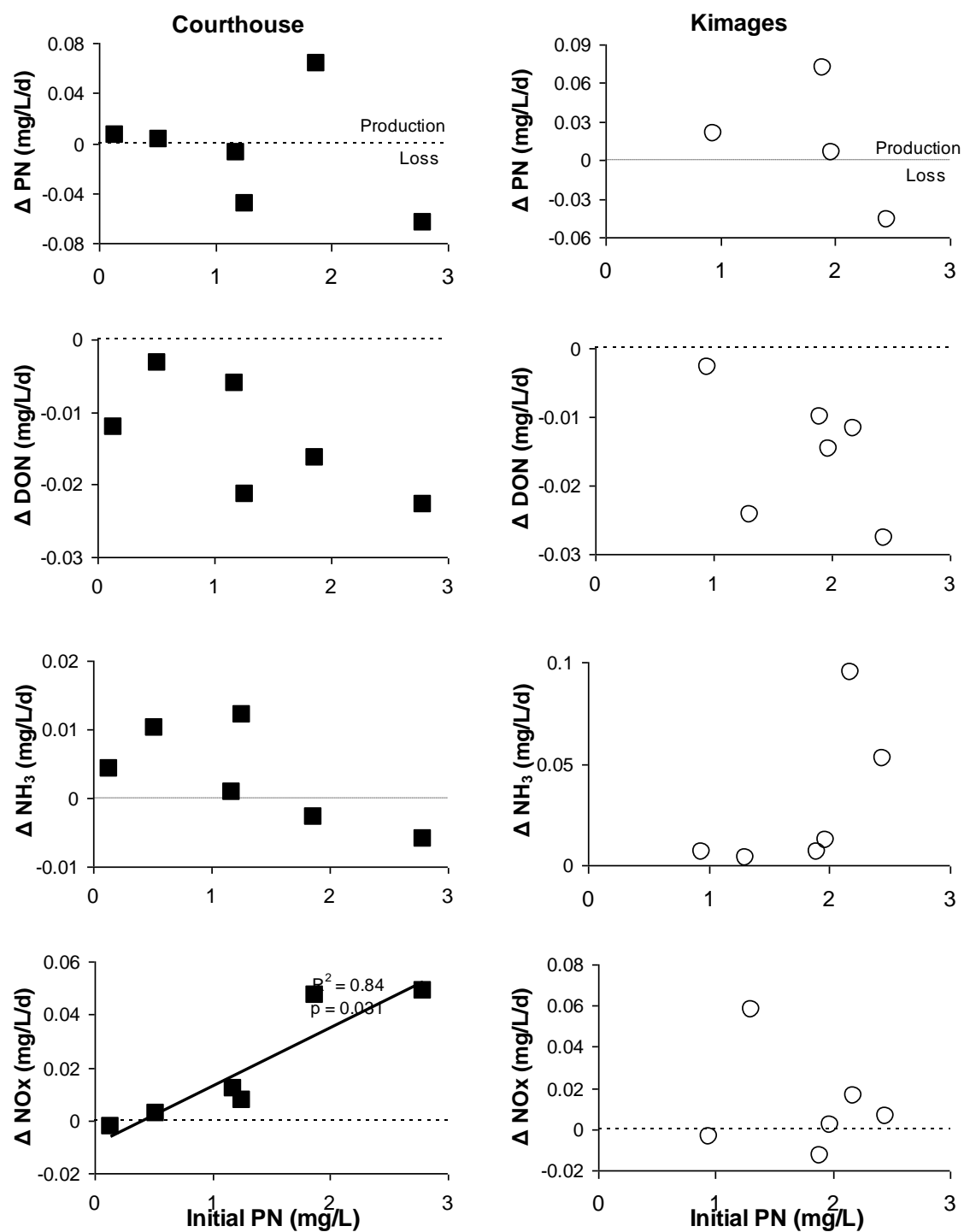


Figure 7. Rates of change in nitrogen fractions and initial particulate nitrogen concentration. Regression line indicates a significant relationship.

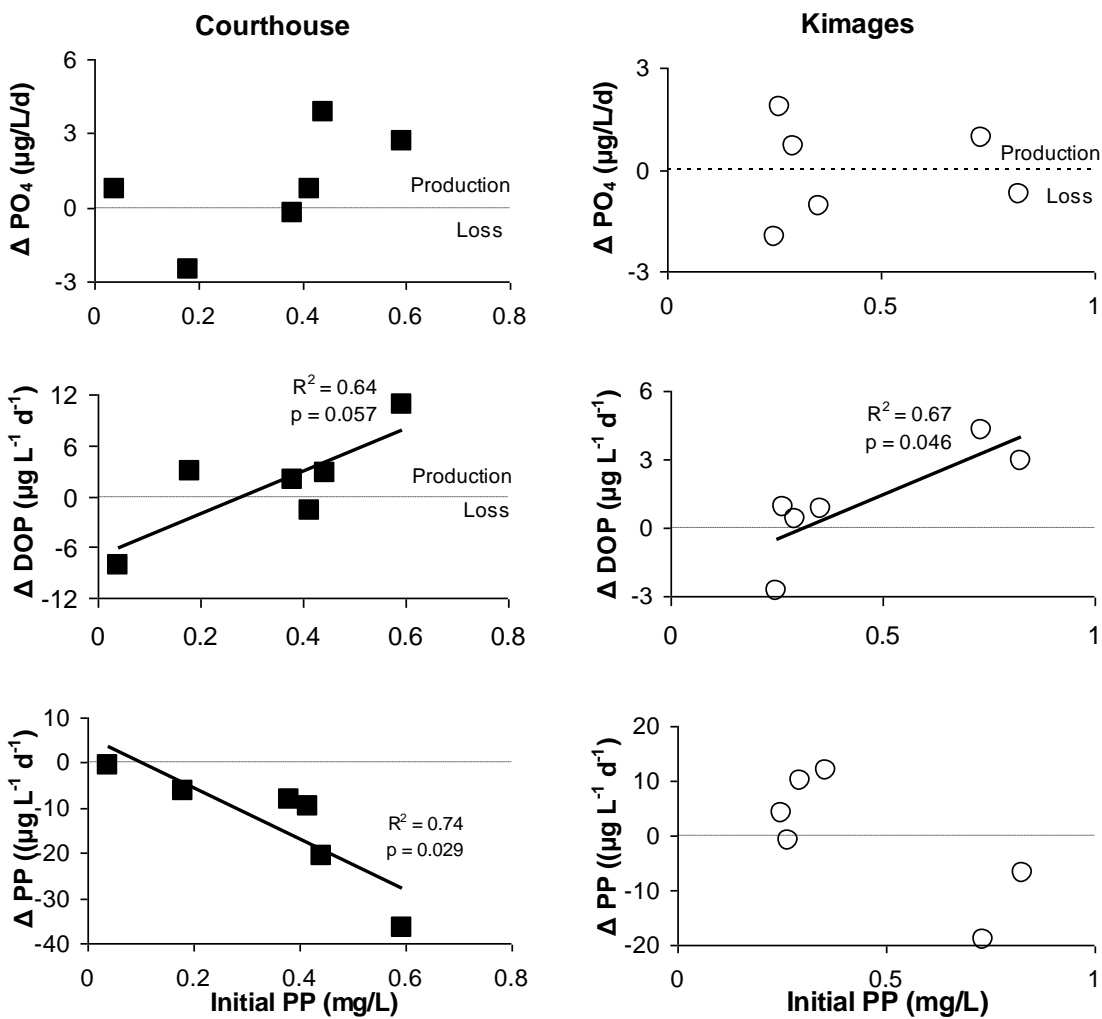


Figure 8. Relationships between initial particulate phosphorus concentration and rates of change in P fractions during 6-day incubations.

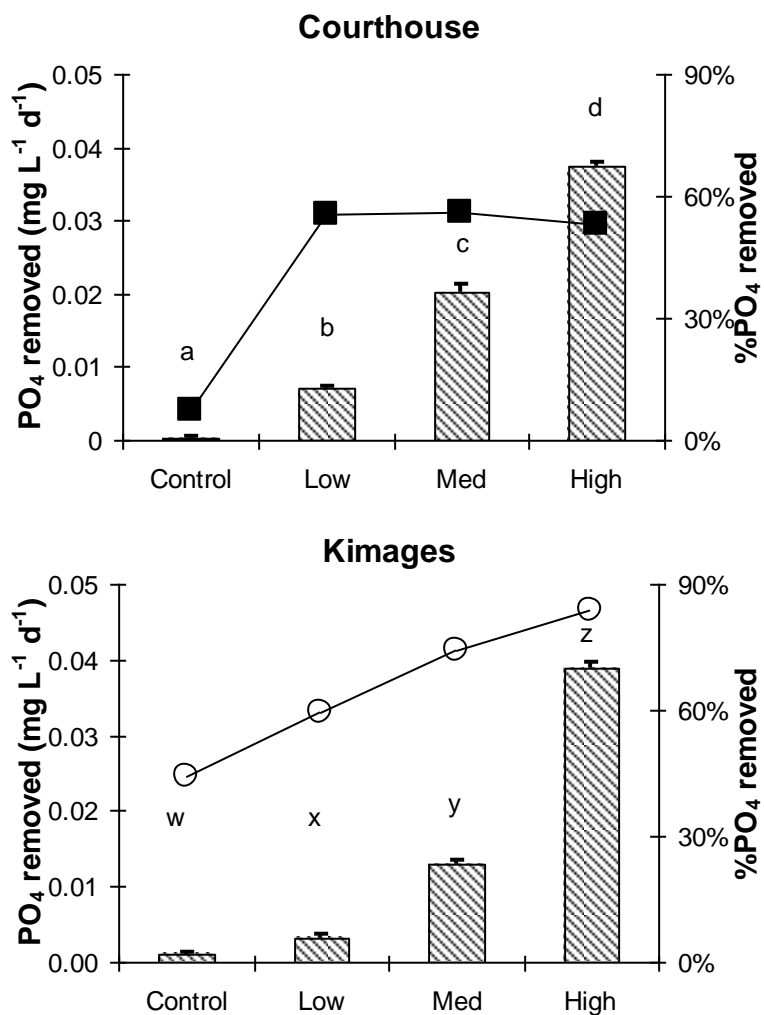


Figure 9. PO₄³⁻ removed from treatment incubations (bars). Letters represent significantly different removal concentrations ($p < 0.005$). Percent of initial phosphate removed from incubations. Dilute treatment data not shown.

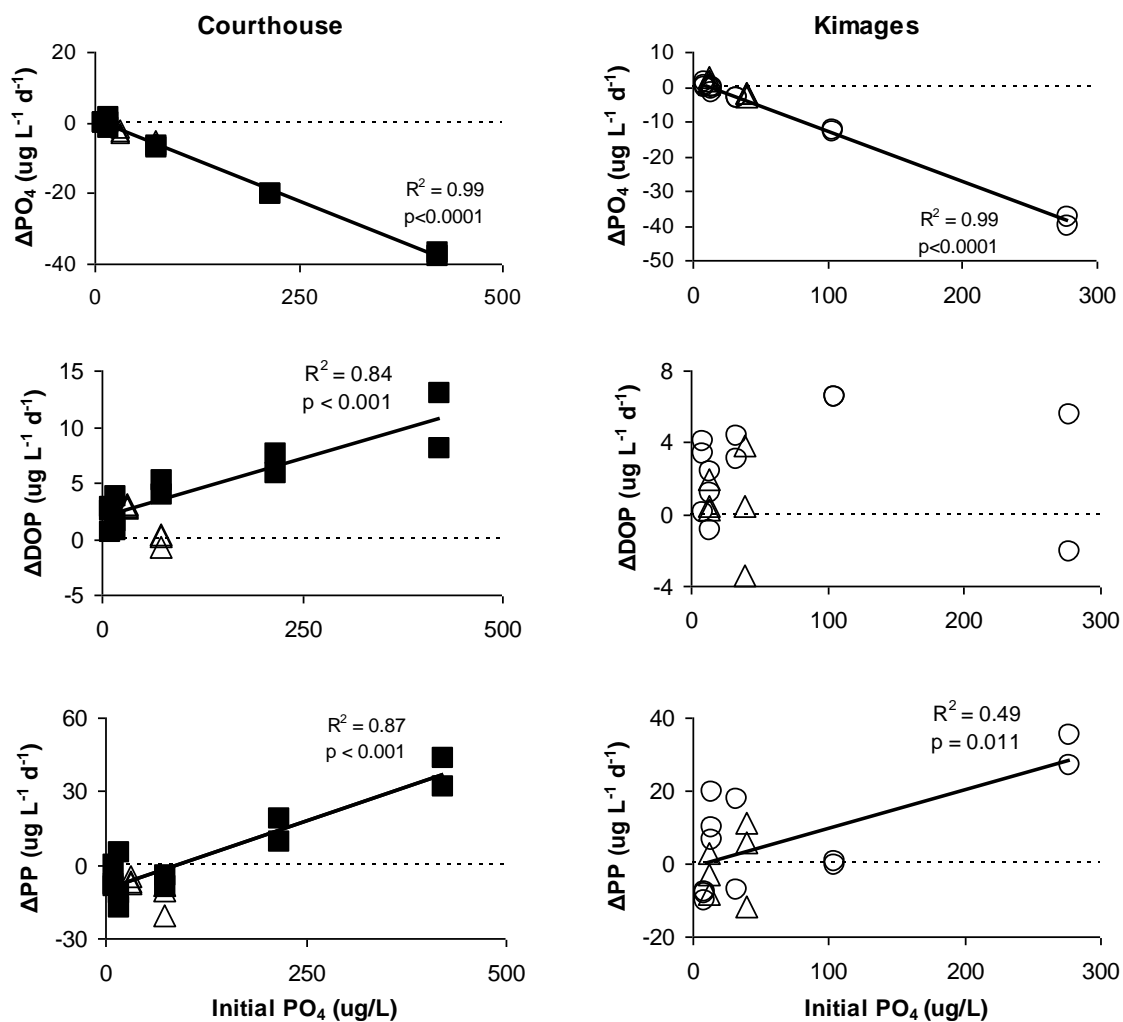


Figure 10. Changes in PO_4^{3-} , dissolved organic phosphorus, and particulate phosphorus concentrations and initial concentrations of phosphate. Open triangles represent data from a prior PO_4^{3-} amendment trial. Note changing y-axes.

Vita

Molly J Sobotka was born on September 1, 1985 in St. Louis, MO where she spent the first 22 years of her life. She received her Bachelors of Arts in Biology from Washington University in St. Louis in 2007. After interning at the St. Louis Zoo for a year, Molly spent six months in a tiny town in southern Missouri following hellbenders (*Cryptobranchus alleganiensis*) all over the place. She then moved to Utah to work with the fish and frogs of the Virgin River and the Great Basin Desert. She began her work at VCU in August 2009. Molly hopes to continue working in stream ecology and to travel as much as possible.